**GEOHERMAL MATERIALS DEVELOPMENT
AT BROOKHAVEN NATIONAL LABORATORY**

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ABSTRACT

As part of the DOE/OGT response to recommendations and priorities established by industrial review of their overall R&D program, the Geothermal Materials Program at Brookhaven National Laboratory (BNL) is focusing on topics that can reduce O&M costs and increase competitiveness in foreign and domestic markets. Corrosion and scale control, well completion materials, and lost circulation control have high priorities. The first two topics are included in FY 1997 BNL activities, but work on lost circulation materials is constrained by budgetary limitations.

The R&D, most of which is performed as cost-shared efforts with U.S. geothermal firms, is rapidly moving into field testing phases. FY 1996 and 1997 accomplishments in the development of lightweight CO₂-resistant cements for well completions; corrosion resistant, thermally conductive polymer matrix composites for heat exchange applications; and metallic, polymer and ceramic-based corrosion protective coatings are given in this paper. In addition, plans for work that commenced in March 1997 on thermally conductive cementitious grouting materials for use with geothermal heat pumps (GHP), are discussed.

INTRODUCTION

The commercial availability of improved and cost effective materials will significantly enhance the ability of DOE/OGT to meet their announced goals

of improving the efficiency of geothermal energy conversion 10 to 20% and reducing drilling and completion costs by 30%. The importance of materials R&D to the geothermal industry was detailed in a study of R&D priorities published in 1994.¹ A panel consisting of representatives from geothermal developers, utilities, consulting firms and contractors assigned a very high priority to corrosion and scaling control. Well completion and lost-circulation control also received high priorities, but at levels below corrosion and scaling. Materials needs exist for specific components such as downhole drill motors, pumps, casing, packers, blow-out preventors, drillpipe protectors, rotating head seals, and heat exchangers. As a result of the small and uncertain geothermal market, industry generally will not develop the special materials required for these critical components on its own. In particular, improvements in lost circulation control, lightweight carbon dioxide resistant well-completion materials, downhole drill motors, and methods for bonding high temperature elastomers to metals for use in drilling components will significantly reduce well costs.

These industrial priorities are being addressed in the Geothermal Materials Development Project. The work consists of laboratory-scale and field testing efforts, the latter performed as cost-shared activities with industry and other national laboratories.

To date, this cooperative R&D effort has resulted in many materials advances that are now used commercially by the geothermal industry. The most

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significant has been in high temperature elastomers. Developed under OGT sponsorship by L'Garde, Inc., the Y-267 elastomer can be classified as a technology breakthrough². Three major U.S. seal manufacturers acquired the technology from the DOE, and molded parts are now commercially available from many firms. The elastomers are widely used in well logging tools, packers, valves, and other equipment. OGT-sponsored work has also been performed to modify Y-267 EPDM to enhance its performance in drillpipe protectors, rotating head seals, and blow-out preventors, and these results were utilized in the Geothermal Drilling Organization (GDO) programs on these components.³

Another successful materials advance was the development of high-temperature polymer concrete formulations.⁴ These materials are now available for use as corrosion resistant linings at temperatures up to 260°C. This development served as the basis for ongoing work on thermally conductive composites, the results from which show promise for use as low cost corrosion and scale-resistant liners for heat exchange applications.

Cements represent another area where considerable progress has been made. The results from this effort currently serve as the basis for the selection of cements used for geothermal well completions throughout the world.⁵ This work also served to elucidate reaction pathways that are now leading to the successful development of lightweight CO₂-resistant cements.⁶ Field testing of these advance materials is expected to commence in the Summer of 1997.

Handbooks published in 1981 and 1983 that summarized the performance of materials in geothermal environments were widely used outputs from the program.^{7,8}

In FY 1996, the Geothermal Materials Program consisted of four activities that are all continuing in FY 1997. These are titled 1) advanced, high temperature, CO₂-resistant lightweight cements, 2) thermally conductive composites, 3) corrosion mitigation at The Geysers, and 4) advanced coating materials evaluations. In addition, a new activity

which focuses on reducing the first cost and improving the efficiency of geothermal heat pumps (GHP) by the development of thermally conductive grouting materials for coupling the heat exchangers in GHPs to the surrounding soil, was started in FY 1997. Descriptions and summaries of the results from each of these activities are given below.

RESULTS

1. Advanced, CO₂-Resistant, Lightweight Cements

The quality of the cementing phase of a geothermal well completion often establishes the life expectancy of the well. Improperly designed cement jobs can result in blow-outs and casing corrosion or collapse. In addition to the need for cements which, upon curing, yield the necessary physical, mechanical and chemical characteristics, their slurry precursors must have rheological properties that permit placement using conventional technology. Low slurry densities (~1.2 g/cc) are desirable to minimize the frequency of lost circulation episodes when attempts are made to cement in weak unconsolidated rock zones that have very fragile gradients.

A recently encountered problem that is severely reducing well life, and has increased costs and environmental concerns, is cement deterioration due to alkali metal catalyzed reactions between CO₂-containing brines and the calcium silicate hydrate (CSH) compounds and calcium hydroxide present in conventional well cements.⁹ In the first case, reactions between Na and K in the brines and CSH phases lead to the formation of substituted CSH compounds such as pectolite and reyerite, both of which are susceptible to carbonation. Leaching of the resulting CaCO₃ and Ca(HCO₃)₂ leads to rapid reductions in strength, increased permeability, and potential corrosion on the outside surface of the well casing. Cement failures attributed to CO₂ are occurring in less than 5 yr, and in one case, resulted in a collapsed well casing within 90 days. Solving these materials problems which could seriously constrain the development of the world's geothermal resources, is the goal of the current cement research activity. Design criteria established by industry and ranked in order of importance are as follows:

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1) compatible with conventional field placement technologies, 2) carbonation rate <5% after 1 yr in brine at 300°C containing 500 ppm CO₂, 3) compressive strength >5 MPa at 24 hr age, and 4) slurry density ≤1.2g/cc. Other important characteristics needed are: 1) life expectancy 20 yr, 2) pumpability of ~4 hr at >100°C, 3) bond strength to steel >70KPa, and 4) H₂O permeability <0.1 m Darcy.

The commercial availability of a well cement that meets the established design criteria will decrease the cost of well completions due to reductions in lost circulation control episodes, increase the life expectancy of wells, and reduce environmental concerns regarding blow-outs. It will also permit development of higher temperature, higher CO₂ content brine resources that are not currently exploitable due to cement deterioration concerns.

Halliburton Services and the Unocal Corporation participate in this Task with BNL on a cost-shared basis. The former identifies retarders for the BNL-developed cements, performs engineering-scale placement tests, makes economic evaluations, and performs mechanical, physical and chemical characterizations to verify that BNL derived data are reproducible. Unocal also conducts validation tests and will provide the well and ancillary equipment for field testing.

Approach

The project consists of five phases: 1) fundamental cement research, 2) mix design, 3) property characterization, 4) placement technology, and 5) downhole evaluations. Phases 3, 4 and 5 are conducted as cost-shared efforts with industry to insure the practicability of the materials and subsequent technology transfer.

Phase 1 consists of fundamental work to synthesize non-portland cement-based materials and to elucidate the interactions that occur between them and a number of lightweight inorganic and organic microsphere fillers. State-of-the-art surface science analytical techniques are used in all parts of this phase. Phase 2 consists of the development of cement-filler mixtures and curing conditions to yield

the desired properties. In Phase 3, the mechanical, physical and chemical resistance characteristics of the most promising formulation are being determined before and after autoclave exposures to CO₂-containing hydrothermal fluids. The technical feasibility for use of the cement slurries in well completions using conventional placement technology is determined in Phase 4. This work includes the selection of retarding admixtures to extend pumpability, and verification of this by the performance of consistometer testing in accordance with American Petroleum Institute (API) Standards. Industrial assistance in the selection of retarders is contributed by a well service company. In Phase 5, which is a cost-shared activity with a well service company and a well owner, the ability to mix and place the cements on a large-scale is verified, and the long-term durability of samples cured in and exposed to downhole geothermal environments is determined.

Status

Cost-shared R&D between BNL, Halliburton Services and Unocal to develop cementing materials produced by acid-base reactions between calcium aluminate cements and phosphate-containing compounds has produced very promising results. Several candidate systems were evaluated with respect to their properties and cost. Studies of the cementing phases formed, microstructure developed, carbonation rate, and changes in strength and permeability after exposure to CO₂ solutions at 300°C were completed. A cement formulation based upon Na₂O, CaO, Al₂O₃, SiO₂, P₂O₅, and H₂O appeared the most promising, and it gave results that met the property and cost criteria necessary for use as a well completion material. As a result, it was tentatively selected for use in a full-scale downhole test to be performed overseas in the Summer of 1997. Plans for testing at the Salton Sea as part of a ongoing GDO program on lost circulation control are currently being formulated. The cement formulation consists of 23.7 wt% Class F fly ash; 15.8 wt% calcium aluminate cement, 31.4 wt% of a 40 wt% sodium metaphosphate solution, and 29.1 wt% Al₂O₃. The latter is in the form of lightweight, hollow ceramic microspheres. This formulation has a slurry density of ~1.2 g/cc, and

after hydrothermal curing forms a strong, CO₂-resistant cement. As an example, a 180-day laboratory test to measure the durability of the BNL cement in high CO₂ brine was completed. In this test, BNL and conventional class G cement samples were exposed in an autoclave to a 4 wt% Na₂CO₃ solution (CO₂ equivalent 15,700 ppm) at 300°C. The results are summarized in Table 1. Data for compressive strength and phase formation are given. As noted, the BNL cement formulation exhibited a strength decrease of 35% to a value of 8.5 MPa within the first 30 days, and then remained constant for the duration of the test. No evidence of reactions between the cement and CO₂ was detected. The reason for the initial reduction in strength seems to be the growth of crystalline hydroxylapatite phases in the analcime layers. The latter are responsible for strength development. Once a well-formed hydroxylapatite phase is present, the strength stabilizes.

In contrast, the conventional lightweight class G cement-based formulation used as a control exhibited a 65% decrease in strength before an apparent leveling off at 5.2 MPa after 60 days. Analyses indicated the formation of calcite (CaCO₃) as a carbonation reaction compound and xonotlite [Ca₆Si₆O₁₇(OH)₂] as the major hydrate product, after exposure for only 7 days. Within 30 days, a major portion of the xonotlite phase had been converted into calcite and pectolite [NaCa₃H Si₃O₉]. Thus, it is apparent that the xonotlite which is responsible for strength development in Class G cement undergoes alkali carbonation degradation;

With prolonged exposure, additional CO₂ will react with the CaCO₃ to form water soluble calcium bicarbonate. Continuous leaching of the latter will result in increased porosity and permeability, and decreased strength.

Based upon these results, it is clearly apparent that the BNL-developed lightweight cement is superior to the conventionally used class G cement when exposed to hydrothermal fluids containing high levels of CO₂.

As mentioned above, the incorporation of the hollow Al₂O₃ microspheres with the cementing matrix yields slurry densities of ~1.2g/cc. It should be noted that these microspheres may not be commercially produced in some overseas regions, and to import them may be cost prohibitive. If so, and/or a slurry density of 1.3 to 1.6 g/cc is acceptable, lower cost nitrogen gas-surfactant agent foaming systems can be used.

2. Thermally Conductive Composites

The economic utilization of binary working fluids in geothermal energy conversion cycles operating in the 150° to 200°C temperature range would dramatically increase the size of the exploitable hydrothermal resource. A significant item of cost in a binary plant is the shell and tube heat exchangers, primarily due to the necessity of using high alloy steel tubing to prevent corrosion. Even then, excessive fouling prevents the economic use of binary processes with hypersaline brines. Both problems could possibly be solved with the development of a suitable liner that could be used on low cost mild steel tubing. Cost effective utilization of bottoming cycles in flash processes as a means of increasing energy conversion efficiency will also become possible.

This Task is performed as a collaboration in which BNL supplies the lined heat exchanger tubes and performs materials analyses. Another DOE national laboratory (first INEL and subsequently NREL) provides a test skid and the thermodynamic analyses. Industry (CalEnergy) provides the test site and operates the test skid.

The technical feasibility for the use of high temperature composite materials for corrosion protection was demonstrated by BNL in the early 1980s, and since then they have been used successfully by the geothermal industry. BNL has patented these formulations.^{10, 11} It was then shown that significant increases in the thermal conductivity of the polymer-matrix composites could be achieved by the incorporation of high conductivity materials

TABLE 1
Cement Durability Upon Exposure to CO₂-Enriched Brine #

<u>Cement</u>	<u>Exposure</u>	<u>Compressive Strength</u>	<u>Phases Present*</u>	
	<u>Day</u>	<u>MPa</u>	<u>Major</u>	<u>Minor</u>
BNL	0	13.1	AN	HOAp, Q, SA
"	7	11.0	AN	HOAp, Q, SA
"	10	9.7	AN	HOAp, Q, SA
"	30	8.5	AN, HOAp	Q, SA
"	60	8.6	AN, HOAp	Q, SA
"	90	8.4	AN, HOAp	Q, SA
"	180	8.5	AN, HOAp	Q, SA
Class G	0	14.5	XO, Q	SA
"	7	11.0	XO, Q	P, SA, CAL
"	10	8.3	XO, Q	P, SA, CAL
"	30	7.6	Q, P, CAL	XO, SA
"	60	6.2	Q, P, CAL	XO, SA
"	90	5.2	Q, P, CAL	XO, SA
"	180	5.2	Q, P, CAL	XO, SA

*AN: analcime, HOAp: hydroxylapatite, Q: quartz, SA: sanidine-shelled microsphere, XO: xonotlite, P: pectolite, CAL: calcite

#Temperature 300°C, CO₂ equivalent 15,700 ppm

(SiC, etc.) as fillers.¹² Conductivities approaching those of Type-410 stainless steel were obtained. It was later shown that the addition of high temperature antioxidants into the composite significantly reduced the rate of scale deposition and adhesion to the surface. Work to develop a low cost, low fouling, replacement material for the high alloy steels used in geothermal heat exchange applications was then initiated. The following design criteria were established: 1) heat transfer and fluid-flow characteristics similar to those of AL-6XN tubing, 2) fouling coefficient <50% of AL-6XN when used in brines typical of the Salton Sea KGRA, 3) cost not more than twice that of mild steel, and 4) suitability of the use of conventional technology for joining PCL tubes to tube sheets.

In FY 1994, a 75-day field test of carbon steel tubing lined with a thermally conductive polymer composite (PCL) was conducted under conditions that simulated those in a bottoming cycle in a multi-stage flash geothermal process. The heat exchanger consisted of four 6-meter lengths of 2.54-cm o.d x

1.24 mm wall tubing lined with a 0.76-mm layer of the PC. The hypersaline brine inlet and outlet temperatures were 108° and 89°C, respectively. Concurrently, AL-6XN control tubes were evaluated under similar temperature, pressure, flow and brine composition conditions.

In FY 1995, analyses of the heat transfer, fouling and corrosion resistance performance of the PCL were completed. The post-test examination indicated that the base metal was fully protected by the lining. In addition, the heat transfer performance and fouling rate of the PCL tubes were similar to those of the high alloy controls. In FY 1996, preliminary design, manufacturing and cost studies for utilizing the composite in full scale shell-and-tube heat exchangers were conducted. These NREL-coordinated results established that contingent upon the development of a cost-effective method for joining PCL tubing to the tube sheets, significant reductions (17 to 65%) in the cost of a heat exchanger could be realized.

Approach

The work is being performed as a collaborative effort between BNL, NREL and private industry (CalEnergy). BNL performs the fundamental and applied research necessary to define high temperature polymer and polymer cement formulations, determines protective coating thickness requirements, and develops methods for the placement of thin, uniform coatings on heat exchanger tubes. Post-field test evaluations are also performed at BNL.

Engineering analyses and heat transfer tests are conducted by NREL. The work includes measurements of heat transfer coefficients, cost estimates, and the management of field testing. They also coordinate manufacturability studies and technology transfer activities.

CalEnergy provides the field test site, operating personnel and ancillary equipment. Tests in an environment typical of that in a bottoming cycle application in a flash process are performed. Design, manufacture method and economic studies are then conducted by a heat exchanger manufacturer and NREL.

Status

Plans for a second large-scale field test of a PCL heat exchanger were formulated in FY 1996 and contractual negotiations are nearing completion.

BNL has continued work to identify methods for improving the surface texture and scale-bonding characteristics of PCLs applied to carbon steel tubing. As part of this effort, fundamental work to elucidate the interactions that take place at PCL- or polymer-scale interfaces was performed. The results from these studies indicate that polymers containing ester, ketone, or ether groups should not be used in PCL formulations. These groups were found to react with divalent cations such as Ba and Ca that are present in geothermal brines. The reactions promote hydrolysis of these groups to form carboxylic acid which subsequently reacts with Ba and Ca hydroxides through general acid-base reaction routes. These form Ba- and Ca- complexed

carboxylate salt derivatives such as $\text{COO}\cdots\text{M}\cdots\text{OOC}-$, where M is Ba or Ca. The formation of these interfacial reaction products results in chemical bonding which enhances the shear bond strength (>7 MPa) of scale on PCL surfaces. The use of polyaryl-type polymers such as polyphenylene sulfide (PPS) should significantly reduce the magnitude of the bonding, and thereby make the use of hydroblasting practical for descaling PCL surfaces. This issue will be addressed in Field Test No. 2 that will be performed in the Summer of FY 1997.

3. Corrosion Mitigation at The Geysers

Corrosion problems at The Geysers have increased as steam pressures decline. These have contributed to decreases in electric power generation, increased operating cost, and safety and environmental concerns. In FY 1990, BNL initiated cost-shared work with geothermal steam producers and electric power generating companies active at The Geysers that focuses on low cost solutions to these difficult materials problems.

Currently four industry-identified materials problems are being researched. These are: 1) erosion and cavitation-resistant liners for steam transmission piping systems, 2) stress corrosion resistant materials for turbine components, 3) low cost corrosion resistant coatings for dry cooling tower applications, and 4) corrosion resistant coatings for vent gas blowers.

Problem 1 is being addressed with the Northern California Power Agency (NCPA). Erosion/cavitation occurs in the transmission piping tees located at the well heads. Pacific Gas and Electric Company (PG&E) problems with turbine components (Problem 2) have necessitated the use of expensive titanium blades, but methods for the retrofit of older turbine rotors are needed so that steam desuperheating can be eliminated. Problem No. 3 now has a low priority with PG&E since the installation of any type of dry cooling tower is probably not economical. Of much higher priority for them is Problem 4, vent gas blower materials. When exposed to moisture saturated gas containing

H₂S, H₂, CH₄, and CO₂ at ~80°C, these cast iron casings fail within two years due to corrosion and erosion.

Based upon our extensive experience, materials, developed at or identified by BNL, are selected and test components supplied by operators at The Geysers are prepared for field evaluations. All BNL in-house laboratory testing in this Task is conducted in steam that simulates the fluid at The Geysers. Testing in brine is conducted in Program Activity No. 4.

Approach

The approach being used to meet the project objectives is to optimize polymer, polymer cement composite and pre-ceramic formulations, previously developed under DOE/OGT sponsorship, for specific end-use applications at The Geysers. The identification of need, performance of prototype and full-scale field evaluations, and subsequent economic studies are performed as cost-shared activities with firms active at The Geysers. In FY 1996, engineering ceramics and metal alloys were added to the types of materials under investigation.

The project consists of three phases:

Phase 1 consists of the identification of specific materials problems, elucidation of the fluid environments, and the selection of candidate materials systems. Laboratory testing under simulated process conditions is then conducted to establish technical feasibility. Based upon these results, modifications to the systems are made to maximize corrosion resistance.

Phase 2 consists of small-scale field testing, and contingent upon these results, prototype component testing.

Phase 3 consists of design studies to incorporate the technology into components, cost estimates, documentation, and the identification of potential commercial suppliers of the new technology.

Status

In FY 1996, laboratory and field testing efforts being performed as cost-shared activities with geothermal companies active at The Geysers were continued. Details for these activities are summarized below:

Piping Systems

In March 1992, two polymer cement (PC) lined 30-cm diameter pipe tees were installed by NCPA in a steam transmission line where the conditions are as follows: flow rate 13,640 kg/hr, temperature 173°C, and pressure 0.83 MPa. Both tees were visually inspected after approximately 12 mo exposure. At that time, some fine cracks and small regions of disbondment of the liner were noted, but in general both tees were in good condition. Therefore, the test was resumed and it has continued without inspection for a total exposure time of 57 mo as of February 1997. Since filters located downstream of the tees which are monitored routinely have not collected any pieces of the PC liner, it is expected that no gross erosion or delamination has occurred.

Dry Cooling Tower Components

Prototype sections of polymer coated finned-tubed heat exchanger tubing were placed into test by PG&E at The Geysers in June 1994. In the test environment, the corrosion rate of carbon steel is approximately 15 mpy. Aluminum corrodes at a lesser but still unacceptable rate. Two metal systems, aluminum fins on stainless steel tubing and electrogalvanized steel on carbon steel tubing are being evaluated. Polyphenylene sulfide (PPS) and vinyl ester resin - trimethylolpropane trimethacrylate, applied to surface modified and "as-received" metal surfaces, were used for corrosion protection. Visual inspections were made after approximately 2, 5 and 10 mo, and no signs of blistering, chalking or delamination were apparent on any of the coated samples. All of the samples were reported to be in an "as new" condition. These tests are continuing, but PG&E has not reported the results from more recent inspections.

Turbine Components

Work to evaluate the usefulness of nickel aluminide (NiAl) alloys and high temperature polymers as corrosion resistive coatings on turbine components is being performed as a cooperative effort with PG&E. In April 1996, samples of turbine blade materials coated with PPS that was chemically bonded to the substrate by use of a zinc phosphate coupling system, were prepared for evaluation in a turbine simulator at PG&E. These tests are in progress.

Concurrent with the above field testing, laboratory evaluations of materials such as NiCoCrAlY, Cr_3C_2 -NiCr and NiAl are underway. Additional materials to be evaluated include Cr_3C_2 , WC-based (e.g., WC-Co, WC-CoCr) and TiC-based coatings. ZrO_2 and TiQ coatings deposited on NiAl using sol-gel synthesis technology will also be studied. Test variables will include placement method and coating thickness. Coating adherence and permeability will be measured.

Vent Gas Blowers

A program was started in FY1997 to identify corrosion resistant coatings for use on the cast iron casings of the PG&E vent gas blowers at The Geysers. Failure of these components due to corrosion and erosion frequently occurs within 2 years. Several potential systems were identified and field testing started in January 1997. An exposure time of 5 to 6 months is anticipated. The coating systems selected for evaluation were NiAl, PPS, ethylene methacrylic acid, and ethylene tetrafluorethylene.

As other materials needs at The Geysers are identified by industrial advisory groups, BNL will initiate R&D directed towards solving those problems.

4. Advanced Coating Material Evaluations

Corrosion and scale deposition continue to adversely affect geothermal plant operating costs, energy conversion efficiency, and utilization factors. To combat corrosion, portland cement-based materials

are sometimes used as liners on brine piping systems, but the alkaline nature of the cements prevents their use with acidic fluids. Other conventional protective barrier materials such as epoxies, polyesters and acrylics, or metallic claddings, are limited by the thermal and/or hydrolytic stability of the plastics, and the costs for the metals.

Since the general utilization of high alloy steels is cost prohibitive for most geothermal plants, current practice is to attempt to minimize corrosion and scale deposition by plant design and subsequent operation that may not be optimum for energy conversion and fluid injection. For example, it is well known that lowering the pH of hypersaline brines can significantly reduce silica scale deposition. This would allow greater temperature differentials across the heat exchangers, reduce plant size and complexity by elimination of the clarifiers, and decrease the amount of potentially toxic waste sludges that must be disposed of at ever increasing costs. Unfortunately, the lowering pH option is constrained by increased corrosion problems that currently can only be solved by the use of prohibitively expensive construction materials. Low cost, acid resistant and hydrothermally stable coating systems that can be used for new plant construction and for the retrofit of existing plants are needed.

Recently, the technical and economic feasibilities for the use of biochemical processes for the treatment of geothermal wastes and mineral recovery have been demonstrated at BNL.¹³ As a result, considerable industrial activity is underway as cost-shared efforts with BNL. Portions of these processes operate with low pH (~1), high chloride content, brine sludges at temperatures up to 80°C. To make these processes cost effective, low cost and corrosion resistant materials of construction are needed.

This Activity was started in FY 1995 and is being performed as a cooperative cost-shared effort with geothermal energy firms.

Approach

The project objectives are being met by the

performance of a multi-phase effort with geothermal energy and/or other industrial partners. In Phase 1, specific coating needs are identified and performance specifications defined. Phase 2 consists of the selection of potential candidate polymer and composite systems developed in other program tasks, and optimization of them for the specified end-use application. Field testing of coupon size samples is conducted in this phase of the effort. Contingent upon these results, potential commercial sources and development partners for the technology are identified in Phase 3. Field testing of coated prototype and full-scale process components at the Salton Sea KGRA and other locations is being conducted in Phase 4. Contingent upon these results, Phase 5 will consist of economic studies and the completion of technology transfer.

Status

A number of high temperature polymer and polymer-matrix composite coating systems are under investigation. These include PPS, ethylene metacrylic acid, and acrylic epoxy polymers; and ethylene tetrafluoroethylene copolymer. In attempts to enhance abrasion resistance, crystalline zinc phosphate compounds and NiAl alloys are being evaluated as coupling systems between metal substrates and the polymer topcoats. Methods such as plasma flame spray, chemical vapor deposition and physical vapor deposition are being considered as technologies for placement of the coatings. Test environments include hypersaline brine at 300°C and pH 1 biochemical reagent solutions at temperatures up to 80°C containing *Thiobacillus ferrooxidans*.

A cost-shared effort with CalEnergy to field test PPS-coated pipe is in progress. Two 61-cm-long sections of 25-cm-diam pipe were shipped to them for field testing at one of their Salton Sea power plants, but to date the test has not been started. The inner surfaces of both pipe sections were first cleaned by grit-blasting. This was followed by the application of a BNL developed zinc phosphate conversion coating, the purpose of which is to enhance bonding between polymer-based topcoating materials and the metal substrate. It also provides corrosion protection. One pipe section was then

coated with two layers of PPS. This is an extremely acid resistant, high temperature (~300°C), highly crosslinked material.

A second pipe has one layer of PPS and an outer layer of a PPS-silicon carbide (SiC) composite over the zinc phosphate. Our goal with the composite is to improve the abrasion resistance of PPS. If the PPS systems are shown to be durable, flame spray applied PPS is a likely candidate for evaluation since the technology is suitable for field use. Therefore, it may be possible to retrofit existing pipelines.

In FY 1997, advanced engineering ceramics such as TiC, TiN, and Cr₇C₃ were included in the investigations. These systems have higher temperature capabilities than polymer-based composites and will be more resistant to abrasion. Their adhesions to metal substrates and the ability to form impermeable, thin (~1 micron), durable coatings are unknown, particularly upon exposure to low pH hydrothermal environments. Potential applications are for well casing, pumps, valves, and other moving parts seeing liquid dominated fluids.

Testing to identify suitable materials of construction for use in process components used in the biochemical treatment of geothermal wastes has been initiated. For use as baseline data, corrosion tests on 316L stainless steel were completed. After 10 weeks exposure to a high chloride, low pH brine at 60°, coupons that were totally immersed or totally in a vapor zone did not show any visible corrosion. Coupons that were partially immersed exhibited pitting corrosion above the liquid level.

Tests on thermal sprayed ethylene methacrylic acid and ethylene tetrafluoroethylene in the same brine were also completed. The total test duration was 18 weeks. The ethylene methacrylic acid coatings showed no visible signs of deterioration other than slight surface staining and some loss of gloss. No disbondment occurred. One of the ethylene tetrafluoroethylene coatings developed blisters at the coating-substrate interface and had poor adhesion at the conclusion of the test. The other ethylene tetrafluoroethylene coating did not exhibit any

disbondment. The variation in performance is probably due to the fact that the blistered coating was the first prepared and the thermal spray parameters may not have been optimal for this polymer. Neither of the ethylene tetrafluoroethylene coatings showed any staining or surface changes. It is concluded that both of these coatings appear suitable for corrosion protection in the studied environment provided that sufficient adhesion is achieved. Further studies on these coatings will examine abrasion resistance and adhesion at elevated temperatures.

Corrosion tests on 316L stainless steel and coated carbon steel coupons exposed to *Thiobacillus ferrooxidans* are also in progress. Slight corrosion of the 316L coupons in the vapour zone has been observed. Immersed coupons appear to be undergoing biofouling. Both coated and uncoated coupons have surface deposits. At the conclusion of the test period, the coupons will be cleaned and inspected for corrosion beneath the biofilm.

5. Geothermal Heat Pump Grouting Materials

The objective of this new activity that commenced in March 1997, is to reduce the first cost of installing the ground coupled heat exchangers in geothermal heat pumps (GHP) by 10 to 20%.

Vertically-oriented ground-coupling devices for GHP systems normally consist of a U-tube arrangement inserted into ~50-m-deep boreholes. The total borehole depth depends on factors such as heating and cooling load, soil type, local climate and heat pump model.

Techniques have been developed for the design and installation of such systems which have resulted in adequate performance, but the cost of installation of these systems has been a barrier to widespread utilization. Ideally, the buried heat exchanger should be designed for minimum length, requiring minimal resistance to heat flow between the circulating fluid and the native soil. The composition of backfill material that is placed around the heat exchanger, along with proper backfilling technique, can have great impact on

exchanger performance. Thermal performance of the heat exchanger could be enhanced throughout the heating and cooling season with the use of a backfill material that has sustained high thermal conductivity, thus providing an efficient thermal bridge between the heat exchanger and the surrounding native soil. For example, analysis conducted by Martinez and Sullivan of SNL has shown that performance can be improved by 15% if the backfill grout is twice as thermally conductive as the surrounding soil or by 25% if the grout is four times as conductive.

If this activity is successful, significant reductions in the installation cost of a GHP and increased unit efficiency will result. Environmental concerns regarding the possible contamination of ground water with metals originating from the conventionally used bentonite grouts will also be eliminated.

Approach

The approach that will be used to meet the project objective will be to first quantify required mechanical, physical and cost criteria for the grouting material. The R&D needed to meet these criteria will then be conducted in three phases. Phase 1 will consist of laboratory studies to identify, characterize and optimize promising formulations with respect to the design criteria. The data obtained in Phase 1 will then be used in performance modeling of GHP systems. Phase 3 will consist of field testing to verify the technical and economic practicality of the advanced grouts with GHPs. Phase 2 and 3 will be collaborative efforts with SNL, the University of Alabama and Oklahoma State University.

Status

As a precursor for the experimental effort, design criteria for advanced grouts were compiled. These are as follows: 1) cost <\$0.21/liter, 2) thermal conductivity dry, 1.9W/m.°K, and wet 2.2W/m.°K, 3) pumpability $\Delta P < 0.69$ MPa through a 61m length of 2.54 cm Tremie tube at 37.7 liters/min, and 4) permeability $< 10^{-7}$ cm/sec.

Although formal experimental work in this activity did not commence until early March 1997, previous work at BNL has established the technical feasibility for meeting the design criteria. This effort studied grouts designed to have the following properties: low viscosity, compatibility with conventional mixing and pumping equipment, environmentally safe, low shrinkage, low permeability, low cost, and readily available constituents. The mix design was based on BNL grout formulations for stabilization and containment of hazardous wastes. A variety of filler materials were evaluated and the thermal conductivities of the product compared with those for conventional bentonite and cement grouts. In addition, admixtures commonly used to enhance the properties of grouts and other cement-based materials were utilized.

The results from these initial studies have been reported.¹⁴ Thermal conductivities between 1.7 to 3.3 W/m.° K in the moist state and 1.4 to 3.0 W/m.° K in the dry state were achieved. Values of 0.56-0.80 W/m.° K were measured for low solids bentonite and cement grouts in the moist state. The bentonite grouts desiccated and cracked on drying and they would effectively act as an insulator in such a condition. Further improvement in the grout thermal conductivity is possible by optimizing the packing fraction and filler content and the use of suitably sized steel fibres.

CONCLUSIONS

The goal of the DOE/OGT-sponsored Geothermal Materials Development Project is to provide the technical and managerial basis for the performance of high payoff materials R&D so that the results are available to industry during plant retrofits and when they commence development of higher temperature and chemically aggressive hydrothermal resources. Materials needs have been defined by inputs from Industrial advisory panels, the GDO, professional societies, and two studies made by the National Research Council.

Corrosion, scale deposition and well completion remain high priority topics, and materials solutions to these problems must become available if the

geothermal industry is to remain competitive in foreign and domestic markets.

Significant progress in materials development has been made since Program Review XIV. With respect to well completion, phosphate-modified calcium aluminate cement-flyash mixtures yield low cost, high strength, CO₂-resistant cements. The incorporation of hollow Al₂O₃ microspheres into the cement matrix yields slurry densities of 1.2 to 1.3 g/cc. The use of nitrogen gas-surfactant agent combinations instead of the expensive microspheres, yields a considerably lower cost product with a slurry density of 1.3 to 1.6 g/cc.

The durability of the cement in high CO₂ (~15,700ppm) content brines was demonstrated in laboratory tests. No evidence of carbonation was observed after a 6 month exposure to a 4 wt% Na₂CO₃ solution at 300°C. Some strength retrogression resulting from phase transformations that occurred within the first 30 days, was noted. Beyond that time, the strength remained constant at ~8.5 MPa for the remainder of the test. This value greatly exceeds the strength criterion for a well cement.

Based upon the above data, the reproducibility of which has been demonstrated by industry, plans have been made to complete wells with the formulations this Summer.

The corrosion-protective capability of thermally conductive polymer composite liners (PCL) applied on carbon steel tubing, has been demonstrated. Studies to reduce the magnitude of the adherence of scale deposited on the polymer surfaces are in progress. As part of this effort, fundamental studies to elucidate the interactions that take place at PCL-, or polymer/scale interfaces were completed. The results indicated that polymers containing ester, ketone or ether groups should not be used in the presence of hypersaline brines. Reactions between these groups and Ba and Ca divalent cations present in the brine result in chemical bonding of the scale to the coating surfaces, thereby making it very difficult to descale using hydroblasting techniques. Plans to substantiate these findings by the field testing of tubing lined with polyphenylene sulfide

(PPS) and a PPS-SiC composite have been made, and the test should commence in the early Summer of FY 1997.

The field testing of several prototype geothermal process components coated with BNL-developed materials systems is in progress at The Geysers and other tests are planned for the Salton Sea KGRA. Three general types of protective coatings; polymers, ceramics and composites are included. Components being tested include piping, dry cooling towers, turbine blades, rotor housings, and vent gas blowers. Coatings for use in biochemical processes for the treatment of geothermal wastes are also being evaluated. In conjunction with these tests, methods for the field application of the coatings are being identified. To date, flame spray techniques have given excellent results.

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